

# MERCURY USE: PAPER MILLS

## Mercury is Potentially Used or Released at Paper Mills in Four Different Areas:

- 1 A component in equipment (e.g., switches, gauges, thermometers)
- 2 An ingredient in chemicals or laboratory chemicals (e.g., thimerosal)
- 3 A contaminant in raw materials (eg., caustic soda)
- 4 An incidental release due to a production process (eg., coal combustion)

## Where Would These Products or Processes Be Found in a Paper Mill?

Mercury-containing instruments and devices are potentially used in a number of places in a typical bleached kraft pulp and paper mill:

- ✓ power and recovery boilers
- ✓ product drying systems
- ✓ instrument shops
- ✓ process laboratories

There are also a number of mercury-containing products that may occur commonly in your facility. Examples of these products include thermostats, light switches, and lamps.

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### ATTACHMENT

Mercury Pollution Prevention at a Bleached Kraft Pulp & Paper Mill

## ABOUT THIS HANDOUT

This is one chapter of the “Wisconsin Mercury SourceBook.” The Sourcebook was written as a guide for communities to help identify and reduce the purposeful use of mercury. The SourceBook contains background information on mercury contamination and provides a seven-step outline for drafting a mercury reduction plan.

This handout is one of the nineteen sectors that were highlighted in the SourceBook as a potential contributor of mercury in any given community.

### What you will find in this handout:

- ★ Information on mercury-containing products and that are unique to the paper industry
- ★ Information on mercury-containing products that are found both in the paper industry and in a wide variety of other sectors (e.g., fluorescent lamps, switches)
- ★ Case studies that describe the source substitution experiences of other paper mills
- ★ Action ideas that describe pollution prevention, recycling, and management practices for a mercury reduction plan for a paper mill. This provides a good overview of the types of mercury-containing products and alternatives that may exist in the paper industry.
- ★ A sample proclamation that explains the mercury issue and possible mercury minimization options for the paper industry
- ★ Current mercury projects in this sector

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For more information, please contact:

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## WHY SHOULD I BE CONCERNED ABOUT MERCURY?

Some of you may remember playing with mercury when you were a child. Its silvery white shimmer was entrancing, and the ability of its glistening mass to split and come back together again was magical. But scientists are now beginning to realize that there is another side to mercury's wily nature. In fact, it is some of mercury's most elemental qualities that make it a difficult substance to handle.

Mercury is a common element that is found naturally in a free state or mixed in ores. It also may be present in rocks or released during volcanic activity. However, most of the mercury that enters the environment in Wisconsin comes from human uses.

Because mercury is very dense, expands and contracts evenly with temperature changes, and has high electrical conductivity, it has been used in thousands of industrial, agricultural, medical, and household applications.

It is estimated that half of the anthropogenic mercury releases in Wisconsin are the result of the purposeful use of mercury. The other half of mercury emissions originate from energy production.

Major uses of mercury include dental amalgams, tilt switches, thermometers, lamps, pigments, batteries, reagents, and barometers. When these products are thrown in the trash or flushed down a drain, the mercury doesn't go away.

The good news is that the majority of products that use mercury purposefully have acceptable alternatives. For example, electric vacuum gages, expansion or aneroid monitors are good alternatives to mercury blood pressure monitors. Mechanical switches, magnetic dry reed switches, and optic sensors can replace mercury tilt switches.

Replacing mercury-laden products with less toxic alternatives is

referred to as *source reduction*. Source reduction allows us to eliminate the use of mercury in certain waste streams. This is especially beneficial considering the volatile nature of mercury, because mercury can so easily transfer from air to soil to water.

Practicing source reduction in combination with recycling the mercury already in the waste stream can have a significant impact on reducing mercury levels in the environment.

## HEALTH EFFECTS OF ELEMENTAL MERCURY

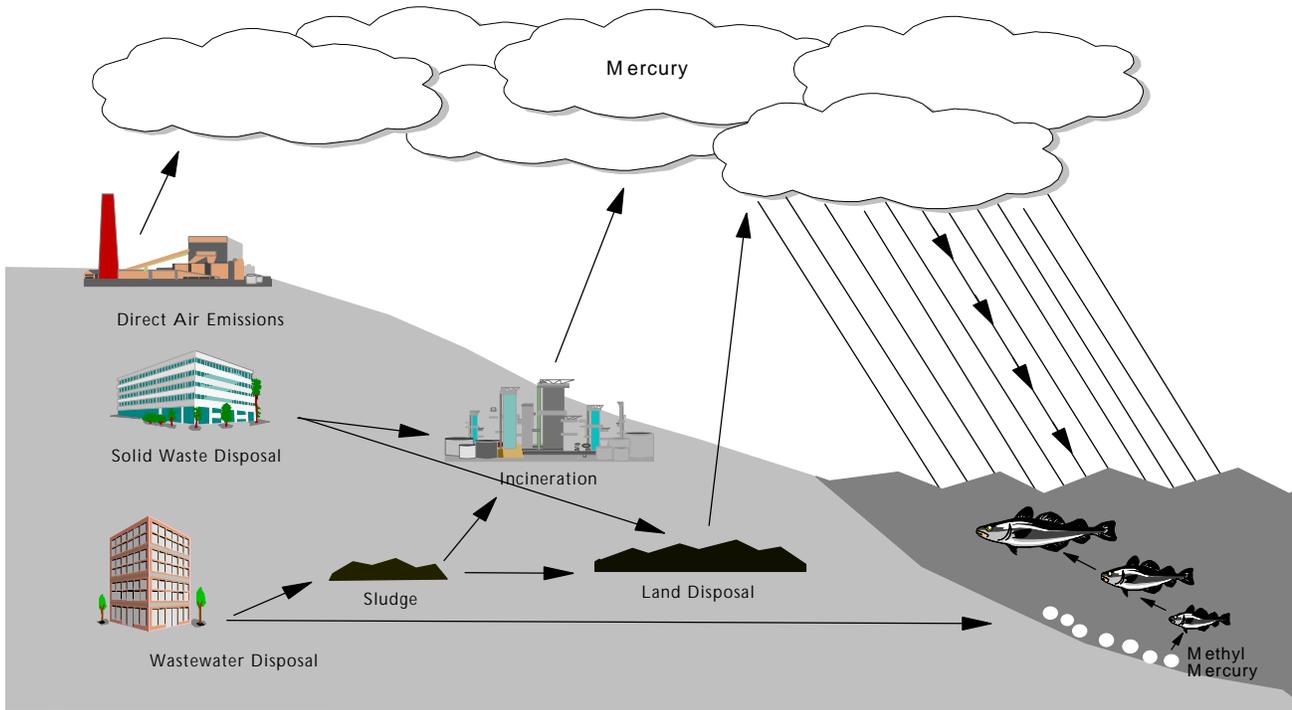
The toxicity of mercury has long been known to humans. Hat makers during the 19th century developed symptoms of shaking and slurring of speech from exposure to large amounts of inorganic mercury, which was used to give a metallic sheen to felt hats. This gave rise to the term "mad as a hatter."

The hat makers were suffering from neurological damage from the inhalation of mercury fumes. Exposure to elemental mercury vapors can cause acute respiratory problems, which are followed by neurologic disturbances and general systemic effects. Acute exposure to inorganic mercury by ingestion may also cause gastrointestinal disturbances and may effect the kidneys.

## SO WHAT'S THE BIG DEAL?

Mercury is a bioaccumulative, persistent, toxic substance that threatens the health of humans and wildlife throughout North America. The USEPA, Environment Canada, the International Joint Commission, the Commission for Environmental Cooperation and many state and provincial governments have identified mercury as one of the most critical pollutants for significant elimination and/or reduction.

## Mercury Transport and Bioaccumulation



Mercury can enter the environment from a number of paths. For example, if a mercury-containing item is thrown into the garbage, the mercury may be released into the atmosphere from landfill vapors or leachate, or the mercury may vaporize if the trash is incinerated. If mercury is flushed through a wastewater system, the mercury will likely adhere to the wastewater sludge, where it has the potential to volatilize and be deposited elsewhere. Mercury can enter the atmosphere through these various means because it evaporates easily. It then travels through the atmosphere in a vaporized state.

Once mercury is deposited into lakes and streams, bacteria convert some of the mercury into an organic form called *methylmercury*. This is the form of mercury that humans and other animals ingest when they eat some types of fish. Methylmercury is particularly dangerous because it *bioaccumulates* in the environment. Bioaccumulation occurs when the methylmercury in fish tissue concentrates as larger fish eat smaller fish. A 22-inch Northern Pike weighing two pounds can have a mercury concentration as much as 225,000 times as high as the surrounding water.

These concentrations are significant when one considers the potential toxic effects of methylmercury. Methylmercury interferes with the nervous system of the human body and can result in a decreased ability to walk, talk, see, and hear. In extreme examples, high levels of methylmercury consumption has resulted in coma or death.

Many animals that eat fish also accumulate methylmercury. Mink, otters, and loons in Wisconsin have been found to have high levels of mercury in their tissue. Mercury can interfere with an animal's ability to reproduce, and lead to weight loss, or early death.

### Fish Consumption Advisories

There are currently 260 lakes and more than 350 miles of rivers in Wisconsin that have fish consumption advisories because of mercury.

Approximately 1 out every 3 sites that is tested is listed on the advisory; no sites have ever been removed.

Forty-eight states now issue fish consumption advisories to protect human health. Most of these warnings are related to mercury contamination.

## Sewer Pipes

Historically, mercury was used widely in industrial processes. Because mercury has a high specific gravity (13.6), it pools in low-lying areas in process wastewater systems. This mercury can settle at a low point such as a sump or trap and remain in the pipes of a paper mill for many years. Often the slow dissolution of the mercury in a sump, trap, or pipe is enough to cause violations of wastewater discharge standards even after poor management practices have been eliminated. Hot spots in a paper mill's piping may appear where equipment maintenance areas were located. Whenever traps or sumps are moved or cleaned, the solid contents should be treated as a hazardous waste unless proven otherwise. For more information, please see the excerpts from the MWRA/MASCO Infrastructure Subcommittee Maintenance Guidebook that appear in the "Resources" section of this sourcebook.

## Keeping Mercury Out of Wastewater

There are a number of ways mercury can enter the wastewater stream of a paper mill. When a mercury-containing product such as a thermometer is broken over a sink or improperly cleaned up after a spill, the mercury could get flushed down the drain. Mercury may also be present in a paper mill's sewer pipes and traps from historical use of mercury.

Once mercury enters a wastewater treatment plant, most of it concentrates in wastewater biosolids during treatment. Since most treatment plants dispose of generated solids by land spreading, mercury enters the terrestrial environment by this process. Some of this mercury spread on land may, over time, be volatilized to the atmosphere. This mercury may then be deposited into lakes and streams, methylated, and ingested by fish, eventually reaching wildlife and humans.

To prevent such occurrences, it is important to have effective spill response measures. Instruments containing mercury should be labeled and proper procedures should be followed when cleaning or refilling instruments that contain mercury. Instrument cleaning or refilling should take place in a well ventilated area, and, if possible, over a tray to contain any spills.

# 1 A COMPONENT IN EQUIPMENT

- ✓ Batteries
- ✓ Detergents and cleaners
- ✓ Gauges and manometers
- ✓ Fluorescent lamps
- ✓ Specialty lamps
- ✓ Switches, relays, and sensors
- ✓ Thermometers
- ✓ Thermoelectric devices
- ✓ Thermostat probes

## Mercury Product Focus: Batteries

- ✓ Mercuric Oxide Batteries

Prior to the 1980s, most primary batteries and some storage batteries contained mercury in the form of mercuric oxide ( $\text{HgO}$ ), zinc amalgam ( $\text{Zn-Hg}$ ), mercuric chloride ( $\text{HgCl}_2$ ), or mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ). Although the amount of mercury used in each of these batteries was very small, the number of batteries sold in the US was enough to make alkaline batteries the largest component of mercury in the solid waste stream in 1989.

Great pollution prevention progress has been made in this field. In the last decade, the US battery industry has achieved a 99 percent reduction in their use of

mercury! The use of alternative materials and different manufacturing techniques have eliminated the use of mercury in almost all battery applications.

Mercury does exist in mercury zinc, carbon zinc, silver oxide, and zinc air batteries. The amount of mercury discarded in mercury zinc batteries is expected to decline in the future as the use of silver oxide and zinc air batteries increases. The use of mercury in zinc air and silver oxide batteries is expected to be discontinued.

Today, mercuric oxide batteries are the only batteries that use mercury to any measurable degree. There are two basic types of mercuric oxide batteries: button cell and larger sizes. The button cell batteries are the types that are most often sold for personal use; they are used in hearing aids, watches, and other items requiring a small battery.

Mercuric oxide batteries offer a reliable and constant rate of discharge. Therefore, the larger mercuric oxide batteries (which look like 9-volt or fat AA batteries) are often used in military, hospital, or industrial uses. The mercury content in these mercury oxide batteries total 33 to 50 percent mercury by weight of the battery.

### 1993 Wisconsin Act 74

The 1993 Wisconsin Act 74 prohibits the sale in Wisconsin of any alkaline manganese battery manufactured after January 1, 1996, unless the manufacturer can prove that the alkaline manganese battery contains no intentionally introduced mercury. Alkaline manganese button cells can only be sold if they contain no more than 25 mg of mercury.

Zinc Carbon batteries manufactured after July 1, 1994 for sale in Wisconsin must contain no intentionally introduced mercury. Beginning July 1, 1994 mercuric oxide batteries, except button cells, may not be sold in Wisconsin unless the manufacturer identifies a collection site that meets prescribed standards, informs each purchaser of the collection site and a telephone number to call for information on recycling batteries, and informs the Department of Agriculture, Trade, and Consumer Protection and DNR of this collection site. The law also states that only a certified collection site may treat, store, or dispose of mercuric oxide batteries, and they must be recycled if possible.

### Batteries and Mercury Content

From "Household Batteries Waste Management Study," by Gershman, Brickner, and Bratton, Inc., 1992; "Managing Used Dry-Cell Batteries: A Household Hazardous Waste Fact Sheet," MPCA

Type of Battery	Example of Use	Mercury Content
<b>Alkaline</b>		
Cylindrical or rectangular cells; the most commonly recognized battery. Labeled "alkaline."	Flashlight, radios, toys, calculators, remote controls, electronic games, portable radios and televisions, garage door openers.	Previously contained an average of 0.5 percent mercury to control the zinc reaction. 1993 Wisconsin Act 74 mandates that all alkaline manganese batteries sold in Wisconsin after January 1, 1996 be mercury free. Alkaline manganese button cell batteries to contain no more than 25 milligrams of mercury .
<b>Zinc Carbon</b>		
Cylindrical or rectangular cells; labeled as "General Purpose", "Heavy Duty" , or "Classic"	Best used in slow drain applications like clocks, garage door openers, pagers, and smoke detectors. Have much shorter life span than Alkaline batteries.	Use of mercury in these batteries is being phased out. 1993 Wisconsin Act 74 mandates that all zinc carbon batteries for sale after July 1, 1994 be mercury free.
<b>Silver Oxide</b>		
Button shaped with no distinguishing marks	Watches, calculators, toys, greeting cards, musical books	Contain about one percent mercury by weight. Mercury use in these batteries is expected to be discontinued.
<b>Zinc Air</b>		
Usually button shaped. Identify by pin hole on one side	Hearing aids	Contain about one percent mercury by weight. Mercury use in these batteries is expected to be discontinued.
<b>Mercury Zinc (Mercuric Oxide)</b>		
Button shaped, marked with + ; larger mercuric oxide batteries look like 9-volt or fat AA batteries	Hearing aids, watches, and other items requiring a small battery. In consumer applications, mercuric oxide batteries are being replaced by zinc-air button cells.  The larger mercuric oxide batteries are often used in military, hospital, or industrial uses.	Contain significant amounts of mercury ; total 33 to 50 percent by weight of the battery.  Wisconsin Act 74, requires a collection system for those selling mercuric oxide batteries, and requires the recycling of mercuric oxide batteries unless no reasonable alternative exists.

## Mercury Product Focus: Detergents & Cleaners

The Massachusetts Water Resources Authority (MWRA), in conjunction with MASCO (a consortium of Longwood Medical and Academic Area Institutions), has been working with their area hospitals and academic institutions to identify and address the problem of mercury contamination in hospital and medical waste streams. As part of this process, the MWRA group also worked to identify “other sources” of mercury contaminants. These are common products, such as bleach, alcohol, laboratory lids, not otherwise thought to be of significant importance or concern, that might contain low levels of mercury. Thus far, a total of 118 products has been identified by this team. This information is applicable in a variety of settings.

### “Other Sources of Mercury”

*Information from the Massachusetts Water Resources Authority/MASCO*

Product	Mercury Content (ppb)
Ajax Powder	0.17
Comet Cleaner	0.15
Lysol Direct	<0.011
Soft Scrub	<0.013
Kodak Fixer	6.9; 3.7
Kodak Developer	2.65; 6.0
Alconox Soap	0.004 mg/kg 0.005 mg/kg <0.0025 mg/kg
Derma Scrub	<5.0 <2.5
Dove Soap	0.0027
Ivory Dishwashing Liquid	0.061
Joy Dishwashing Liquid	<0.01
Murphy’s Oil Soap	<0.012
Soft Cide Soap (Baxter)	8.1
Sparkleen Detergent	0.0086
Sunlight Dishwashing Detergent	<0.011

## Mercury Product Focus: Gauges - Manometers, Barometers, and Vacuum Gauges

*(from blue waste connection pamphlet)*

- ✓ Air flow measurement devices using a Pitot Tube and manometer (may also be called an airway controller)
- ✓ Commercial-industrial manometers

Paper mills may encounter liquid mercury in the gauges found in manometers or vacuum gauges. The mercury in these gauges responds to air pressure in a precise way that can be calibrated on a scale.

Mercury-free alternatives to these gauges operate on the same principle as these gauges but use mercury-free liquids in the tube.

Needle or bourdon gauges operate under a vacuum with a needle indicator. Electronic gauges can be used to measure pressure, but they must be calibrated with a mercury manometer. Equipment manufacturers recommend that service technicians use a needle or digital gauge to test the systems they are servicing, but that they calibrate the gauges they use in the field with a mercury manometer kept at their shop.

Mercury manometers occasionally need servicing to maintain their accuracy, and elemental mercury often remains as a waste. If the manometer is hard to read because of dirt and moisture in the tube, the mercury needs to be removed and replaced.

## Mercury Product Focus: Lamps

- ✓ fluorescent
  - bilirubin blue
  - general purpose straight, U-bent, circline, compact
  - high output
- ✓ germicidal lamps
  - cold cathode
  - hot cathode
  - slimline
- ✓ metal halide
- ✓ high pressure sodium

There are a number of electric lamps that use mercury as an intrinsic part of their functioning. These lamps include fluorescent, mercury vapor, metal halide, and high pressure sodium lamps. These lamps may be used indoors or outdoors in heat lamps, film projection, photography, dental exams, photochemistry, water purification, or street lighting.

Fluorescent lamps contain mercury in a vapor form. The electric current of the lamp “excites” the mercury atoms, which then give off invisible ultraviolet light. The ultraviolet light then “excites” a powdery phosphorus coating inside the tube that emits visible light. The mercury that is contained in these lamps is emitted into the atmosphere when the lamps are broken, disposed of in landfills, or incinerated.

Fluorescent lamps are still a good option. They last longer and cost less to run than incandescent lights because they use up to 50 percent less electricity. This energy savings helps reduce mercury emissions because small amounts of mercury are present in coal that is burned in power plants. The less energy we use, the less mercury will be released into the environment when coal is burned.

## Recycling Your Fluorescent Lamps

Several Wisconsin companies are in the business of recycling fluorescent lamps and incandescent bulbs. The copper coils, and aluminum or brass end pieces are smelted and reused as raw materials for non-food products. The glass can be purified and used to make fiberglass. The mercury is distilled from the phosphor powder and reused in new lamps and thermometers.

State hazardous waste regulations prohibit businesses from disposing of waste lamps and light bulbs in sanitary landfills if those lamps and bulbs contain levels of heavy metals that exceed hazardous waste limits. For information on the storage, collection, and transport of fluorescent lamps, please see the informational handout, "Recycling Your Fluorescent Lamps," in the "Resources" section of this sourcebook.

## New Low Mercury Fluorescent Bulb

Phillips Electronics has developed a long-life fluorescent that contains so little mercury it is no longer considered a hazardous waste. "Typically fluorescent lamps have an overabundance of mercury, because mercury loses its effectiveness due to physical and chemical reactions. So manufacturers put in an overdose of mercury to compensate for these reactions," said George Preston, a scientist at Philips Lighting Co. Currently, a four-foot lamp contains about 22.8 milligrams of mercury, down from 38.4 milligrams in 1990. Philips's new lamp contains less than 10 milligrams of mercury. The new lamp, named ALTO™, relies on a "buffering mechanism" that blocks the physical and chemical reactions that cause the mercury to lose its effectiveness over time. The lamp also uses a new form of phosphorus patented by Philips.

*From "Philips Unveils a Fluorescent Lamp With Less Mercury and a Long Life," Wall Street Journal, June 9, 1995*

## Types of Bulbs and Lamps that Contain Mercury

- ◆ **Fluorescent Lamps** - the tube-style were first used as overhead lighting in offices, now they also come in compact globe shapes for a variety of home and office uses
- ◆ **Mercury Vapor Lamps** - the first high intensity discharge (HID) lamps with blue-white light, originally used as farmyard lights
- ◆ **Metal Halide Lamps** - newer, more efficient HID lights found in homes and offices
- ◆ **High-Pressure Sodium Vapor Lamps** - white-yellow HID lights used for street lamps and outdoor security lighting
- ◆ **Neon Lamps** - brightly colored lamps typically used in advertising; most colors contain mercury except red, orange, and pink

*- From the Wisconsin Recycling Markets Directory*

## Mercury Product Focus: Switches and Relays

### Displacement/Plunger Relays

*Mercury to Steel or Tungsten Contact; Mercury to Mercury Contact*

- ✓ industrial process controllers
- ✓ high current/voltage lighting
- ✓ power supply switching
- ✓ resistance heating
- ✓ tungsten lighting
- ✓ wetted reed relay/wetted reed switch: test, calibration, measurement equipment

### Tilt Switches

*Including SPST, SPDT, NO, NC, wide angle, omnidirectional, circuit board mount*

- ✓ "man down" alarms
- ✓ airflow/fan limit controls
- ✓ fluid level control
- ✓ pneumatic tube communication systems
- ✓ pressure control
- ✓ safety shut off- limit switches for industrial machinery
- ✓ temperature control

Another source of mercury that paper mills may encounter is mercury switches. A small electrical switch may contain 3,500 milligrams of mercury; industrial switches may contain as much as eight pounds of mercury. Mercury is used in temperature-sensitive switches and in mechanical switches. The mechanical (tilt) switches are activated by a change from a vertical to a horizontal position. These are used in products like thermostats and silent switches. Mercury-containing tilt-switches may also be present in or under the lids of clothes washers and chest freezers - they stop the spin cycle or turn on a light. Mercury tilt switches are also found in motion-sensitive and position sensitive safety switches in clothes irons or space heaters. If a mechanical switch is not visible in these items, a mercury switch is probably being used.

Mercury tilt switches have been used in thermostats for more than 40 years. According to Honeywell, Inc., a major manufacturer of thermostats, more than 50 million mercury-containing thermostats have been sold since the 1950s for use in homes and offices. Mercury in these thermostats provide accurate and reliable temperature control, require little maintenance, and do not need a power source. However, each mercury switch in a thermostat contains about 3 grams of mercury. (There may be one or more of these switches in a single thermostat, each switch in a sealed glass bulb.) Alternatives to these products include electronic thermostats, which can be programmed to set room temperatures at predetermined time (*blue brochure: the waste connection*)

Float control switches may be used in septic tank and sump pumps to turn the equipment on and off when water is at a certain level. Often, these switches are visible. Temperature-sensitive switches may be used in thermostats. Yet another type of mercury switch, the plunger or displacement relay, is used in high current, high voltage applications that could include lighting, resistance heating, or power supply switching (*M2P2*).

## Reduction Works!

Honeywell Corporation has been running a free take-back program in Minnesota to collect any brand of used mercury-containing thermostat through either a reverse distribution system or a recycle by-mail system.

Honeywell works with heating, ventilating, and air-conditioning (HVAC) wholesalers who sell their products. Honeywell has one license (called a network license) for all the wholesalers who are participating as a consolidation point for the thermostats. HVAC wholesalers contact their Honeywell customer service representatives to order containers for used thermostats, and Honeywell sends the wholesaler a plastic container with an attached lid that holds 100 thermostats.

Homeowners who replace their own thermostats without contractor assistance or with contractors who are not currently participating in the Honeywell program may recycle their thermostats through the free recycle-by-mail system. These individuals can call a toll-free number to receive a free postage paid thermostat mailer.

### Mercury Switches in Electrical Applications

(source: Michigan Mercury Pollution Prevention Task Force, 1996)

Switch	Quantity of Mercury	Available Alternatives
<b>Tilt Switch</b>		
· Thermostats	3,000 - 6,000 mg	Electronic type and snap switches
· Float Control (septic tank and sump pumps)	?	Magnetic dry reed switch, optic sensor, or mechanical switch
· Freezer Light	2,000 mg	Mechanical switch
· Washing Machine (power shut off)	2,000 mg	Mechanical switch
· Silent Switches (light switches prior to 1991)	2,600 mg	Mechanical switch
<b>Thermo-Electrical Applications</b>		
· Accustat (“mercury in glass thermostat,” a calibrated device resembling a thermometer is used to provide precise temperature control for specialized applications)	~ 1,000 mg	?
· Flame Sensor (used in residential and commercial gas ranges, mercury is in capillary tube when heated mercury vaporizes and opens gas valve or operates switch. Used for both electrical or mechanical output.)	2,500 mg	Hot surface ignition system for devices or products that have electrical connections.

## Mercury Product Focus: Thermometers

- ✓ ASTM and laboratory
- ✓ cup case
- ✓ incubator/water bath
- ✓ Mason's Hygrometer
- ✓ maximum registering
- ✓ minimum/maximum
- ✓ sling psychrometer
- ✓ tapered bulb
- ✓ weather

Digital or aneroid thermometers are good alternatives for most applications of mercury thermometers.

## Mercury Product Focus: Thermo-electric Devices

Mercury column movement opens and closes an electrical circuit at a preset or adjustable setpoint.

- ✓ mercury in glass thermal switch with integral or remote mounted solid state control
- ✓ mercury in glass thermostat tubes and devices
- ✓ thermoregulator
- ✓ thermostat sensor with stainless steel capillary tube

## Mercury Product Focus: Thermostat Probes (also known as mercury thermocouples)

*(from blue waste connection pamphlet + draft text)*

### Mercury Flame Sensor/Mercury Safety Valve

- ✓ "cycle pilot" devices
- ✓ some furnaces
- ✓ some infrared heaters

Mercury-containing thermostat probes may be found in several types of gas-fired appliance that have pilot lights such as ranges, ovens, clothes dryers, water heaters, furnaces, or space heaters. The metal probe consists of a metal bulb and thin tube attached to a gas-control valve. The mercury is inside the tube and expands or contracts to open and shut the valve. A high percentage of gas stoves, ovens, and space heaters contain a mercury thermostat probe. Electric stoves and hot water heaters (gas, electric, and oil) may contain mercury thermostat probes.

Mercury thermostat probes, also known as flame sensors or gas safety valves, are most commonly present as part of the safety valve that prevents gas flow if the pilot light is not lit. In this application the bulb of the thermostat probe projects into or near the pilot light. These are commonly present in gas ovens and may be present in any other appliance with a pilot light.

A mercury-thermostat probe may also be present as part of the main temperature controlling gas valve. In this application, the probe is in the air or water that is being heated and is not directly in contact with any flame. These are typically found in older ovens, clothes dryers, water heaters, or space heaters.

## 2 MERCURY AS AN INGREDIENT IN CHEMICALS OR LABORATORY CHEMICALS

Chemical reagents, used with regularity in a wide range of laboratory testing, are likely sources of mercury contamination.

The difficulty of identifying which chemicals and reagents contain mercury is compounded by the fact that Material Safety Data Sheets (MSDS) are not required to list the hazardous components of a product unless that component is present at a level of  $\geq 1\%$  (0.1% for carcinogens). This means that a particular product *could* contain up to 10,000 parts per million of mercury before the manufacturer would have to alert users of that fact.

*(MWRA operations subcommittee final report)*

### Work by the MPCA

John Gilkeson of the Minnesota Pollution Control Agency has compiled an extensive list of all mercury-containing compounds that are currently available for research and scientific purposes. He has developed a list of all mercury-containing compounds with a CAS number. These charts are attached at the end of this "educational institutions" chapter.

A number of facilities have discovered that mercury is present in very low levels in some of their products. However, because the mercury was added as a preservative, not as an active ingredient, its low level may be below the reporting threshold and thus not included in the Material Safety Data Sheets (MSDS) sheets.

*(gilkeson + butterworth, Metpath)*

### Mercury-Containing Chemicals and Alternatives

*compiled from City of Detroit, Gilkeson, Terrane, Michigan m2p2*

Chemical	Alternative
Mercury (II) Oxide	Copper catalyst
Mercury Chloride	None Identified
Mercury (II) Chloride	Magnesium Chloride/Sulfuric Acid or Zinc Formalin, Freeze drying
Mercury (II) Sulfate	Silver Nitrate/Potassium/Chromium-(III) Sulfate
Mercury Nitrate (for corrosion of copper alloys) for antifungal use (mercurochrome)	Ammonia/Copper Sulfate Neosporin, Mycin
Mercury Iodide	Phenate method
Sulfuric Acid (commercial grade; mercury as impurity)	Sulfuric acid from a cleaner source
Zenker's Solution	Zinc Formalin

**Work by The Massachusetts Water Resources Authority**

**Reagents: The Mercury Products Database**

The Massachusetts Water Resources Authority (MWRA), in conjunction with MASCO (a consortium of Longwood Medical and Academic Area Institutions), has been working with their area hospitals and academic institutions to identify and address the problem of mercury contamination in hospital and medical waste streams. The Operations Subcommittee of this group set out to identify mercury in reagents. As part of this process, a database worksheet was developed to capture the wide range of information known to contain mercury. Next, a letter was sent to 153 major reagent vendors to elicit supplier support in identifying the trace levels of mercury contained in their products. The letters also requested that suppliers provide verification of product mercury content via the submission of a state certified laboratory report.

Using all available inputs, a total of 5,504 products were identified and inventoried into the master database using both vendor and member responses to requests for information. The statistics for their findings are as follows:

Total number of products inventoried: .....	5504
Number of records that contain mercury data: .....	781
Number of records that contain mercury concentrations below detection (BD): .....	166
Number of records with mercury concentrations BD - 1 ppb: .....	43
Number of records with mercury concentrations 1 - 5 ppb: .....	53
Number of records with mercury concentrations 5 - 10 ppb: .....	19
Number of records with mercury concentrations > 10 ppb: .....	469
Number of records under review of concentration data: .....	31

Due to the size of the overall Mercury Products Database, only that portion of it which contains chemicals and products that have been verified, as of 8/21/95, to contain mercury at some level, have been included in the attached report.

**75 Priority Samples**

In an attempt to maximize the value of the database, MWRA selected seventy-five (75) of the most commonly used products by member hospitals and institutions and tested these for mercury content.

The analysis results for the 75 priority samples appear on the following page.

## Results from 75 Priority Samples

*Information from The Massachusetts Water Resources Authority (MWRA), in conjunction with MASCO (a consortium of Longwood Medical and Academic Area Institutions)*

Product Sampled	Mercury Content (ppm)
Seven Deionized Water Samples	<0.0010
Periodic Acid	<0.0010
Acetone	<0.0010
Sodium Iodate	<0.0010
Acetonitrile	<0.0020
Aluminum Potassium Sulfate	<0.0010
Boric Acid	<0.0010
Butter Solution pH -7	<0.0010
Fixer	0.0049
Formaldehyde	0.012
Glutaraldehyde	<0.0010
Herpes Buffer	<0.0010
Phosphate Buffered Saline	<0.0010
Potassium Carbonate	<0.0010
Sodium Carbonate	<0.0010
Sodium Sulfate	0.010
Sodium Bisulfate	<0.0010
TDX	<0.0020
TRIS	<0.0010
Triton X-100	<0.0010
Oxalic Acid	<0.0010
Sodium Phosphate Dibasic	<0.0010
3%, 30% Hydrogen Peroxide	0.0012
Isopropyl Alcohol	<0.0010
Nitric Acid	<0.0019
Potassium Chloride	<0.0010
Silver Nitrate	<0.0010
Sodium Bicarbonate	<0.0010
Sodium Chloride	<0.0010
Trizma Buffer	<0.0010
Sodium Phosphate Monobasic	<0.0010

# 3 A CONTAMINANT IN RAW MATERIALS

## Caustic Soda

Manufacturing plants may use chlorine, caustic soda, or muriatic acid to treat water or to assist in the production of paper products, cosmetics, pharmaceuticals, or food products. Manufacturing plants may dilute sodium hydroxide or potassium hydroxide and use it to regenerate ion exchange resin, adjust the pH of water or process feedstocks, or in their intermediate or final processes. Additionally, caustic soda may be used to treat “cooling” water used in power plants and boilers.

The Chlorine Institute, the trade association of chlor-alkali manufacturers, has recently supported an initiative set forth by the Virtual Elimination Project to reduce mercury emissions from mercury-cell chlor-alkali manufacturing by 50% by the year 2005. The Institute has also supported a 50% reduction in the deliberate use of mercury (purchases or consumption) in chlor-alkali manufacturing by 2005.

These significant commitments are an important step in reducing mercury emissions in the US. We applaud the efforts set forth by the Institute and support their voluntary actions of environmental leadership.

*from a memo addressed to Ms. Elizabeth LaPlante of the USEPA from Robert Smerko, president of the Chlorine Institute, dated September 19, 1996.*

## Chlorine Production and the Mercury Cell Process

*(From November 21, 1994 C&EN)*

The mercury process is one of three electrolytic systems that convert sodium chloride in brine into chlorine and sodium hydroxide, which is referred to as caustic soda. In the US, about 75% of chlorine is made in diaphragm cells, 13% in mercury cells, and 11% in ion-exchange membrane cells. The remainder is formed as a by-product of other chemical reactions.

In mercury cells, liquid mercury forms the cathode, gathering sodium ions from brine to form a mercury-sodium amalgam. Chlorine gas is released at the anode. The amalgam, when transferred to a “decomposer” and reacted with water, produces sodium hydroxide solution, hydrogen gas, and mercury, which is returned to the electrolytic cell.

As US chlorine production is consolidated, small mercury-based plants are the most likely to close. In Europe, most chlorine production is based on mercury cells, but the European Union plans to phase out their use by 2010. And Japan already has replaced most mercury cells, says Roger E. Shamel, president of consulting Resources Corp., Lexington, Mass., because of incidents of mercury poisoning.

Diaphragm cells produce chlorine, hydrogen gas, and sodium hydroxide solution in one cell, with no mercury involved. brine flows into an anode compartment, which is separated from the cathode by a diaphragm. Chlorine forms at the anode, and the sodium ions and dilute brine traverse the diaphragm. Hydrogen is released at the cathode, and the sodium hydroxide-salt solution is removed. The effluent is concentrated by evaporation, and salt precipitates.

Ion-exchange membrane cells, the newest method, allow nearly one-step chlor-alkali production. As in the diaphragm cells, brine flows into the anode compartment, where chlorine is formed. But the membranes selectively allow only the sodium ions to pass into a water-filled cathode compartment. The cathode solution is removed from the cell and concentrated.

The table below shows the estimated mercury concentration (ppb) in wastewater given the usage of caustic (in tons per day) and the average wastewater discharge (in gpm).

Mercury in Wastewater (ppb)				
	Wastewater Flow (gpm)			
Caustic Used (tons per day)	100	500	1,000	5,000
1	0.017	0.003	0.0016	0.0003
2	0.033	0.007	0.0033	0.0007
10	0.17	0.033	0.016	0.0033
20	0.33	0.066	0.033	0.0066

*Table from Vulcan Chemicals*

## REDUCTION WORKS!

### Case Study: Potlatch Corporation - Tracking Down Mercury in Feedstock Chemicals

Potlatch Corporation is a pulp and paper manufacturing facility in Cloquet, Minnesota that produces high line coated papers. The plant changed its bleaching process to Elemental Chlorine Free (ECF) in March, 1994, which required the introduction of new feedstock chemicals in the bleach plant. Ultimately, it was discovered that the new chemical was contributing to occasional spikes of mercury in the mill's wastewater, which is discharged to the Western Lake Superior Sanitary District in Duluth.

In mid-1994, a Mercury Pollution Prevention Task Force, consisting of representatives from Potlatch,

the local POTW, and the University of Minnesota-Duluth, was formed to investigate chemicals used in the process.

Caustic soda feedstock was tested and eliminated because the company was no longer using mercury grade caustic soda. However, the testing of sulfuric acid revealed that some shipments had low mercury levels, while other shipments were higher. The use of high mercury sulfuric acid correlated with the mercury peaks in Potlatch effluent. Further investigation revealed that the low and high mercury sulfuric acids were from different manufacturing processes. The company then took

the step of informing suppliers that the company had to be assured of low mercury content on all its feedstock chemicals.

“Worst Month” vs. “Best Month” reductions were about 7.5 pounds of mercury for this facility!

*(taken directly from “Mercury Reduction Through Treatment Chemical Selection,” a handout for the Lake Superior basin Energy Efficiency Workgroup Meeting, 2/27/96 + ncasi bulletin board oct 11 95)*

Carri Lohse-Hanson at the Minnesota Pollution Control agency has undertaken a project of “Mercury Reduction Through Treatment Chemical Selection.” She has researched mercury levels in caustic soda (see chart below) and has also found that other feedstock chemicals may have high levels of mercury. for example, sulfuric acid produced at a lead smelter was found to have significantly higher levels of mercury than sulfuric acid made from a copper smelter.

The Mercury Reduction Through Treatment Chemical Selection project will collect information on sources and characteristics of feedstock chemicals, including the prices of various grades, and will identify likely users of these materials. The second phase of the project will distribute information and request switching to low mercury feedstocks.

The following table from the Minnesota Pollution Control Agency provides preliminary information on characteristics of different grades of caustic soda:

<b>Characteristics of Different Grades of Caustic Soda</b>					
<b>Properties*</b>	<b>Mercury Cell</b>	<b>Membrane Cell</b>	<b>Rayon Grade</b>	<b>Diaphragm Grade</b>	<b>Purified</b>
sodium hydroxide	50%	50%	50%	50%	50%
sodium chloride	400 ppm	100 ppm	100 ppm	11000 ppm	300 ppm
sodium chlorate	3 ppm	5 ppm	3 ppm	3000 ppm	10 ppm
sodium carbonate	1000 ppm	1000 ppm	1000 ppm	2000 ppm	1000 ppm
sodium sulfate	100 ppm	250 ppm	250 ppm	500 ppm	500 ppm
iron	3 ppm	3 ppm	3 ppm	10 ppm	5 ppm
nickel	--	0.3 ppm	0.3 ppm	3 ppm	4 ppm
copper	--	0.3 ppm	0.3 ppm	0.2 ppm	0.2 ppm
mercury	0.25 ppm	0.001 ppm	0.2 ppm	0.001 ppm	--
heavy metals	1.5 ppm	5 ppm	15 ppm	10 ppm	10 ppm
silica	17 ppm	10 ppm	15 ppm	50 ppm	80 ppm

*\* Maximum values  
Information from The Minnesota Pollution Control Agency*

## Sulfuric Acid

The Mercury Pollution Prevention Task Force at the Potlatch Cloquet mill discovered some interesting things about sulfuric acid. Here is what they report:

Although sulfuric acid can be produced using raw sulfur, it is widely produced from the byproduct sulfur dioxide that is captured to reduce air emissions in the petroleum and metal smelting industry. Mercury typically enters these processes with mined materials and is incidentally released with stripped sulfur dioxide gas. The Potlatch investigation revealed typical mercury levels in sulfuric acid that was produced from a variety of sources. Here are their findings, from lowest mercury levels to the highest:

It is important to note that the above findings only reflect a snapshot in time of product testing that occurred in a particular location. Other facilities that have tested their sulfuric acid have found high mercury levels from petroleum refineries. Therefore, the Potlatch results may not reflect mercury levels across all facilities at all times. It is best to have your own sampling done or to have your supplier provide you with documented information.

### Sulfuric Acid Mercury Concentration from Various Suppliers to the Potlatch Cloquet Mill

Manufacturing Process Byproduct Of	Mercury Concentration (Mg/L)
Secondary Lead Smelters	1 - 10
Secondary Copper Smelters	0.01 - 0.1
Petroleum Refineries	0.001

# 4 MERCURY AS AN INCIDENTAL RELEASE DUE TO A PRODUCTION PROCESS

## Industrial Boilers

Mercury is present in coal, oil, natural gas, or wood used in electric steam generating units. Mercury is emitted as trace contaminant when volatilized at high temperatures.

Another potential source of mercury related to boilers is “cooling water “ used to treat water used in power plants or boilers. This water is often treated with pH-altering chemicals, such as caustic soda and sulfuric acid. If the caustic soda was made with a mercury cell process, there may be high levels of mercury in its wastewater.

## MERCURY SPILLS

It is essential to handle mercury and mercury-containing items safely. Small droplets of spilled mercury may lodge in cracks and sinks, mix with dust, accumulate on work surfaces, and adhere to knit fabrics, shoe soles, watches, gold, and other jewelry. This allows for mercury to potentially be transported to other locations, homes, or businesses.

### The Costs of Mercury Spills

Mercury spills can be expensive for a number of reasons. Here are some examples:

#### The Cost of Clean-up

- ◆ A mercury-containing sphygmomanometer broken on a carpeted floor at Butterworth Hospital cost \$2000 to clean up.

#### Labor costs

- ◆ It took Riverside Hospital 8 to 16 hours to clean up a mercury spill (the mercury had fallen in tile crevices).

#### Facility Down-Time

- ◆ The room in which a mercury spill occurs will be unavailable for use until the site is decontaminated. Riverside Hospital found that their room was out of service for at least one day.

#### Equipment Loss

- ◆ A mercury-containing switch in an oven in a University of Michigan Hospital cafeteria exploded. It cost \$3500 to clean up the spill. The oven, a \$25,000 piece of equipment, was irreparably damaged.

#### Training Time

- ◆ Continuing to use mercury containing items can be expensive for your facility because of the needed staff training for spill response plans. However, if you are still using mercury-containing products, don't neglect this important step! An improperly handled spill can end up costing even more to decontaminate.

### **Handle Mercury Safely!**

- ✓ Use mercury only in uncarpeted, well-ventilated areas. Provide troughs on smooth surfaced tables and benches to collect mercury spills. Reserve the room for mercury use only; restrict traffic in the area.
- ✓ Ask workers to remove all watches and other jewelry - especially gold jewelry since mercury readily combines with gold - and have them wear a mercury vapor respirator and protective clothing: gloves, disposable gowns, and shoe coverings.
- ✓ Prohibit smoking, eating, and drinking in the area.
- ✓ Train all workers to understand the properties and hazards of mercury and to carry out safe handling procedures and specific policies related to mercury disposal.
- ✓ Clean and calibrate all mercury-containing equipment according to the manufacturer's recommended handling procedures and the formal procedures posed by your communications or safety program supervisors.
- ✓ Ask your safety supply vendor for a mercury vacuum sweeper and spill cleanup kit. Having the right equipment on hand will limit the amount of mercury released into the atmosphere.

- From "The Case Against Mercury: Rx for Pollution Prevention," The Terrane Institute

## ACTION STEPS FOR PAPER MILLS TO CONSIDER

### Product Substitution

- ✓ Contact each chemical supplier you use for material feedstock (e.g., caustic soda, sulfuric acid) and request a mercury analysis of the product or a certification that the product is mercury free.
- ✓ If you find a chemical solution that contains a significant amount of mercury, contact the supplier for an alternate material.
- ✓ Eliminate the use of mercury thermometers.
- ✓ Eliminate the use of mercurochrome from first aid test kits.
- ✓ Replace mercury-containing compounds or reagents in your laboratories with mercury-free alternatives.
- ✓ Substitute zinc air or silver oxide batteries for your mercuric oxide (mercury-zinc) batteries.
- ✓ Use safe, non-mercury cleaners and degreasers in laboratories and maintenance areas.
- ✓ When remodeling or replacing old equipment, replace thermostats containing mercury switches with thermostats containing electronic type and snap switches, and replace “silent” light switches with mechanical light switches.
- ✓ Examine the use of mercury-containing switches in your facility. Consider replacing these switches when replacing old equipment or remodeling:

#### Tilt Switches

Including SPST, SPDT, NO, NC, wide angle, omnidirectional, circuit board mount

- “man down” alarms
  - airflow/fan limit controls
  - fluid level control
  - pneumatic tube communication systems
  - pressure control
  - safety shut off-limit switches for industrial machinery
  - temperature control
- ✓ Purchase septic tank and sump pumps that contain magnetic dry reed switches, optic sensors, or mechanical switches instead of mercury tilt switches.
  - ✓ Research your use of plunger or displacement relays; consider replacing these relays with mechanical switches.

#### Displacement/Plunger Relays:

- industrial process controllers
- high current/voltage lighting
- power supply switching
- resistance heating
- tungsten lighting
- wetted reed relay/wetted reed switch: test, calibration, measurement equipment

- ✓ Examine use of other mercury-containing products in your facility and consider the alternatives for these:
  - generators
  - high intensity lamps
  - manometers
- ✓ Purchasing departments need to know the cost of alternatives and the suppliers for the alternatives. They should consider disposal costs when evaluating a product; total product cost should include disposal costs and costs for cleaning up accidents.
- ✓ Consider the use of an Administrative Directive, either formal or informal, to end the purchase of mercury-containing products.

### Loss prevention and housekeeping

- ✓ Label instruments containing mercury.
- ✓ Be sure workers are familiar with the laboratory's policies on the proper disposal practices when working with mercury solutions in a laboratory.
- ✓ Follow proper procedures when cleaning or refilling instruments that contain mercury. Instrument cleaning or refilling should take place in a well ventilated area, and, if possible, over a tray to contain any spills.
- ✓ Establish effective spill response measures to ensure the mercury already in your facility is handled in a safe and proper manner. To minimize the risk of an accidental spill, never handle mercury over a sink. The educational program for spill prevention and cleanup should be visual and simple. You may want to consider purchasing and showing a video.
- ✓ Clean or flush the traps, sumps, and pipes in your sewer lines to rid your facility of historical uses of mercury. See excerpts from the MWRA/MASCO Infrastructure Subcommittee Maintenance Guidebook that appear in the "Resources" section of this sourcebook for more information.

### Recycling

- ✓ Establish a battery collection program.
- ✓ Continue to use fluorescent lamps! Even though fluorescent lamps contain mercury, they are a good choice because they use much less energy than regular bulbs. Consider the use of low-m fluorescent lamps; recycle your fluorescent lamps currently in use. Try not to break these lamps because some of the mercury will escape into the air.
- ✓ Recycle or dispose of mercury-containing products in your facility in an environmentally sound manner.

## SAMPLE PROCLAMATION

*Your facility may wish to formally declare your commitment to mercury reduction. You may use the proclamation below, or adapt it to suit your needs.*

WHEREAS mercury is an elemental substance, that once released into the environment, easily and rapidly changes forms to several organic and inorganic states that transfer from soil to air to water and back again;

WHEREAS the organic form of mercury, methylmercury, bioaccumulates in aquatic ecosystems to magnify concentrations in animal tissue in increasing degrees up to 250,000 times;

WHEREAS methylmercury, the most toxic form of mercury, can affect the reproductive efforts of top predators in aquatic environments such as loons, otters, mink, and panthers;

WHEREAS the neurotoxic effects of high levels of methylmercury poisoning in humans has been established, and low-level doses of methylmercury consumption can potentially effect human health, especially that of a fetus;

WHEREAS elemental mercury is a highly toxic substance which can vaporize easily and cause both acute and chronic health effects including severe respiratory irritation and damage to the central nervous system;

WHEREAS mercury has been identified internationally as a toxic substance of concern, and mercury contamination has led to fish consumption advisories for more than 235 lakes and 350 miles of rivers in Wisconsin;

WHEREAS the majority of mercury entering Wisconsin comes from anthropogenic sources, and one-quarter of these emissions are the result of the purposeful use of mercury;

WHEREAS mercury is used widely in consumer and industrial products, where, in most cases, alternative, mercury-free products are available;

WHEREAS pollution prevention or product substitution is a progressive approach to protecting the environment that eliminates or minimizes the generation of mercury-bearing waste, making it one of the most favorable strategies for maintaining a clean environment;

WHEREAS pollution prevention for mercury can help environmental conditions, as well as protect the health and safety of workers;

WHEREAS recognizing mercury minimization as an active opportunity to improve the environment of Wisconsin and the environment of our business, we, the undersigned, do hereby declare our business to be a mercury minimization participant;

WE commit to research the following mercury minimization opportunities in our facility and implement those we find most feasible:

**Product Substitution**

- ◆ Research chemical solutions used for material feedstock. Use a low-mercury alternative if a mercury contamination is discovered.
- ◆ Eliminate the use of mercury thermometers.
- ◆ Eliminate the use of mercurochrome from first aid test kits.
- ◆ Replace mercury-containing compounds or reagents in your laboratories with mercury-free alternatives.
- ◆ Substitute zinc air or silver oxide batteries for your mercuric oxide (mercury-zinc) batteries.
- ◆ Use safe, non-mercury cleaners and degreasers in labs, housekeeping departments, and maintenance areas.
- ◆ Examine the use of mercury-containing switches and consider replacing any mercury-containing items with non-mercury alternatives when replacing old equipment or remodeling:
- ◆ Purchase septic tank and sump pumps that contain magnetic dry reed switches, optic sensors, or mechanical switches instead of mercury tilt switches.
- ◆ Research your use of plunger or displacement relays; consider replacing these relays with mechanical switches.
- ◆ Examine use of other mercury-containing products and consider the alternatives for these:
  - generators
  - high intensity lamps
  - manometers
- ◆ Consider the use of an Administrative Directive, either formal or informal, to end the purchase of mercury-containing products.

**Loss Prevention and Housekeeping**

- ◆ Label instruments containing mercury.
- ◆ Familiarize workers with the laboratory's policies on the proper disposal practices when working with mercury solutions in a laboratory.
- ◆ Follow proper procedures when cleaning or refilling instruments that contain mercury.
- ◆ Establish effective spill response measures to ensure the mercury already in the facility is handled in a safe and proper manner.

Recycling

- ◆ Establish a battery collection program.
- ◆ Continue to use fluorescent lamps! Research the use of the new Alto™ bulb.
- ◆ Recycle or dispose of mercury-containing products in your facility in an environmentally sound manner.

\_\_\_\_\_  
Facility

\_\_\_\_\_  
Name

\_\_\_\_\_  
Date Signed

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*The information included in this pamphlet is essentially a compilation of the best mercury pollution prevention work to date. Information was gathered from the documents below; some material may have been quoted directly from these sources:*

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“Waste Household Battery Management in Wisconsin,” SHWEC Waste Education Series

“Wisconsin Recycling Markets Directory,” Wisconsin DNR, May 1995

## *Current Mercury Work – Paper Mills/Printing*

Specific Outreach/Research	
<b>Project:</b>	<i>Potlach Mercury Pollution Prevention Project</i>
<b>Description:</b>	Identification of mercury sources in pulp mill wastewater; source reduction pilot at Potlach
<b>Agencies working on this project:</b>	Potlach University of MN - Duluth
<b>Project:</b>	<i>Targeted Initiative: Paper Mills</i>
<b>Description:</b>	Study of increased mercury discharge from a recycling plant. Identified plastics as a possible source of mercury
<b>Agencies working on this project:</b>	WLSSD